A New NIST Service for Calibrating Water Permeation Tubes

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NIST is uniquely capable of substantially improving the performance of permeation tube moisture generators (PTG) by calibrating permeation tubes using NIST's trace humidity standard, the Low Frost Point Generator (LFPG). The LFPG is an extremely stable, well-characterized source of humidity whose output is based on invariant thermodynamic properties of water [1]. The expanded uncertainty *(k=2)* of the LFPG is 0.8% water vapor mole fraction [2]. This document describes a new calibration service for water permeation tubes. The service will become available by the end of 2001.

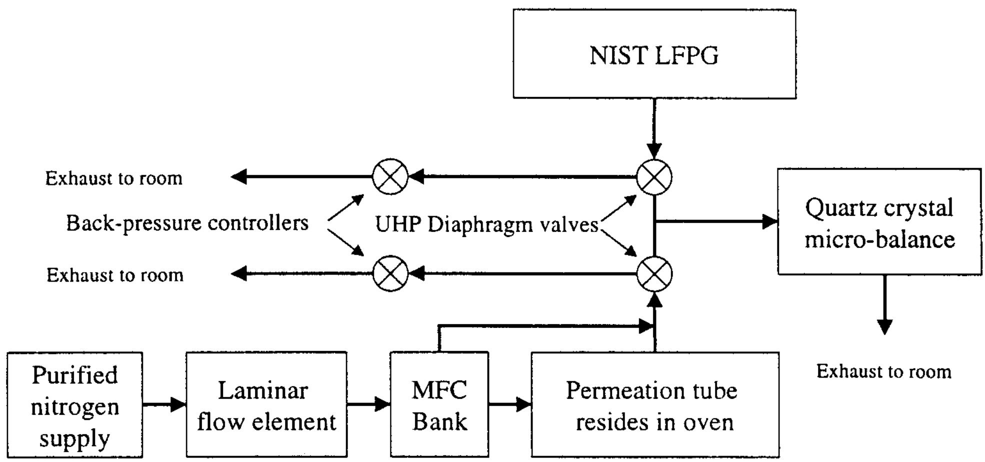
Permeation tube moisture generators are commonly used by the semiconductor industry as portable transfer standards for the calibration of hygrometer systems. The PTG technique uses flow dilution to produce a constant humidity level in a flowing gas stream. Under conditions of constant temperature, water vapor diffuses at a constant rate from the surface of a permeable tube containing liquid water, and this water vapor mixes with a metered stream of dry carrier gas. Assuming steady state and complete mixing of the two gas streams, the expected mole fraction of water vapor in the gas stream at the output of the PTG is,

$$x = \frac{molar\ permeation\ rate\ of\ water}{molar\ flow\, rate\ of\ the\ carrier\ gas} + x_{bg}\ .$$

The molar permeation rate of water is specific to a particular permeation tube and is usually determined by gravimetric methods. Since the permeation rate is sensitive to permeation tube temperature, permeation tubes are housed in a temperature-controlled environment with stability on the order of ±0.1 °C. PTGs are designed to operate at fixed temperature and variable molar flow rate of the carrier gas, usually controlled by a series of mass flow controllers. In this manner, the flow rate is varied to adjust the mole fraction x. For completeness, the above equation also includes the term x_{bg}, which represents any residual water vapor that might be present in the "dry" diluent gas.

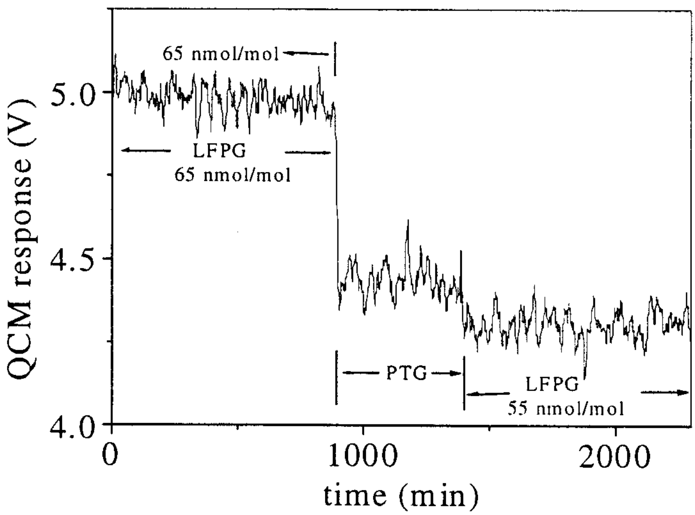
The uncertainty in x produced by the PTG technique is dependent on the uncertainty in permeation rate, uncertainty in the flow rate of the carrier gas, plus the background water vapor x_{bg}. The effect of the x_{bg} on the overall uncertainty is greatest at low parts per billion (ppb) values. For example, a value of 1 ppb for x_{bg} results in a 10% increase in mole fraction at nominally 10 ppb, whereas the contribution reduces to only 1% for 100 ppb. Uncertainty in the carrier gas flow rate is most problematic at the highest ppb values generated by a PTG where carrier gas flow rates are low compared to the maximum flow rate allowed by the mass flow controllers employed by the PTG. In this operating condition, the uncertainty in flow rate, usually specified as a fraction of the full scale flow capability, becomes quite large. While the effects of x_{bg} and the uncertainty in carrier gas flow mostly affect the accuracy of PTGs at the operational limits, the relative uncertainty in permeation rate is constant over the entire operating range of the PTG. Substantial uncertainties in permeation rate (on the order of 10%) are not unusual. The NIST permeation tube calibration service specifically addresses permeation rate uncertainty.

Permeation rate calibrations at NIST are performed using the test rig shown in the accompanying schematic figure. This figure depicts a manifold, constructed of ultra-high purity components, that allows convenient humidity measurement of test gases produced by either the LFPG or by a PTG containing a permeation tube with an uncharacterized permeation rate. The PTG consists of a laminar flow element (LFE) mass flow standard, two mass flow controllers (MFCs), and a temperature controlled oven, which houses the unknown permeation tube. Purified nitrogen flows through the upstream LFE, before being split into two flows by the MFCs. The smaller fraction of the gas enters the oven and flows over the permeation tube, mixing with water vapor that diffuses through the permeation tube wall. The wetted gas recombines with the second, larger gas stream downstream of the oven. Diverting a small portion of the flow through the oven offers the advantage of reducing the oven heat load and improving the oven temperature uniformity. The recombined gas stream is then exhausted into the room environment through a semiconductor-grade back-pressure regulator. When desired, a fraction of the total flow through the test rig PTG is sent to the analyzer for measurement. The LFPG output similarly exhausts to the room, with a fraction available for measurement as needed. Both the LFPG and the unknown sides of the manifold are maintained at nominally the same pressure. A quartz crystal micro-balance (QCM) hygrometer measures the output of either the LFPG or the unknown. The QCM instrument was chosen for its speed of response and short-term stability. A more detailed discussion of the test rig and the measuring technique outlined in the following paragraph can be found in [3].



Measurements are performed as follows. The temperature within the test rig's permeation tube oven is adjusted to the customer's desired temperature. The gas flow through the test rig PTG is adjusted to minimize the effect of x_{bg}, while still supplying adequate gas flow through the manifold. The LFPG is adjusted to produce a mole fraction slightly different from the value expected from the PTG, based on the tube manufacturer's nominal permeation rate and the diluent flow rate. The manifold is switched so that the analyzer measures the output from the LFPG. Once equilibrium is achieved, the manifold is switched to measure the output from the PTG. During this time, the LFPG is adjusted to produce a mole fraction bracketing that produced by the PTG. Once the analyzer reaches equilibrium, the manifold is again switched to the LFPG. The actual mole fraction produced by the PTG is determined by interpolation between the bracketing LFPG test points. A permeation rate for the unknown tube is then calculated. Provided that the hygrometer has a linear response and exhibits little drift over the measurement time interval, the bracketing technique yields a result that is independent of the hygrometer responsivity. Thus, this approach eliminates any dependence upon the hygrometer's internal reference and the need for re-zeroing the sensor. For these reasons, we note that other hygrometers exhibiting good linearity, sufficiently rapid response and low short-term drift would be suitable for this application.

The accompanying figure depicts a typical measurement set. The initial and final H_2O mole fractions were 65 ppb and 55 ppb, respectively, and induced QCM responses bracketing that of the unknown stream. Fluctuations in the QCM output (standard deviation of ~0.04 V) had a period ranging from 20 to 50 min and were driven primarily by temperature fluctuations in the QCM system.



The accuracy of permeation rates calibrated using the NIST LFPG is substantially improved compared to current gravimetric permeation rate determinations. The diluent gas flowing through the test rig is measured by a laminar flow element mass flow standard. The uncertainty *(k=2)* of commercially available laminar flow elements is 0.2% of the flow. The uncertainty of the water vapor mole fractions produced by the LFPG is 0.8% [2]. The measurement uncertainty of the interpolation technique has been demonstrated to be on the order of 1% [3]. The contribution of x_{bg} over the expected calibration range is expected to be less than 2%. Adding these uncertainties in quadrature yields an expected expanded uncertainty in permeation rate calibrations *(k=2)* of 2.4%.

The major contributor to this uncertainty is the water vapor background contained in the diluent gas.

In addition to improved accuracy, NIST calibration of permeation tubes offers other advantages. NIST calibration will be quick, with an expected turnaround time of two weeks. NIST permeation tube calibration will be cost effective, with the required labor per tube expected to be about 5 man-hours. Most importantly, NIST calibration is versatile. Since the permeation rate of water through permeation tubes is independent of the dry gas composition, high accuracy NIST trace humidity standards can now be disseminated to secondary standard humidity generators employed in both inert and corrosive gas service.

NIST permeation tube calibrations will provide competitive advantages to the semiconductor industry. Fabrication facilities, gas suppliers, and analyzer manufacturers can now have greater confidence in the composition of their process gasses, and in the accuracy of their instrumentation and measurements. For more information on NIST permeation tube calibrations, and special tests of analyzers, humidity sensors, and humidity generators, contact:

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